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Interpollutant emission trading of ozone precursors in southeast Texas

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Abstract Interpollutant trading (IPT) allows for trades among emissions of different compounds that contribute to ambient concentrations of the same pollutant. Shortages of single pollutant offsets have motivated the consideration of interpollutant offsets for ozone precursors on a case-by-case basis in California, but IPT has been approached with caution because of the difficulties in assessing the adequacy and uncertainty of trading ratios between oxides of nitrogen (NO_x) and volatile organic compound (VOC) sources and in resolving fundamental environmental policy and equity concerns. This study examines trading of NO_x and VOC emissions in Houston, Texas. Houston annually experiences ozone concentrations that are among the highest in the United States. The region has a large population base as well as numerous petrochemical facilities that emit large amounts of VOCs, including highly reactive VOCs such as ethylene, propylene, and 1,3-butadiene. IPT ratios can be defined as tons of VOC emissions equivalent to a ton of NO_x, given an impact index such as maximum ozone concentration, area exceeding a threshold ozone concentration, or population exposure. IPT ratios for Houston exhibit variability due to a combination of large spatial gradients in emissions and meteorological conditions across the region. NO_x disbenefits have a particularly important influence on the variability in IPT ratios between source categories and metrics on some episode days. IPT ratios based on different impact indices, notably, maximum daily 8-h ozone concentration and population exposure, in Houston correlated poorly with each other, which increases the complexity of trading program design. The results suggest the importance of careful assessment and design of IPT programs.

Keywords Emissions trading · Ozone · Ozone precursors · Urban air quality · Process analysis

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Introduction

Two general forms of emission trading systems predominate in the United States: (1) offsets and (2) multisource cap and trade programs or allowance trading. Offset programs are used in areas that are designated as being in nonattainment of National Ambient Air Quality Standards (NAAQS). In an offset program, new or expanding sources of emissions must be offset by additional emission reductions from existing sources. The primary objective of offsets is to allow continued economic growth and activity in a nonattainment area without increasing emissions that could negatively affect air quality. In contrast, in conventional cap and trade programs, facilities are allocated emission allowances and are able to sell, buy, and bank allowances in accordance with program guidelines. Total emissions in the area (the cap) are reduced over time by lowering the number of allowances.

Cap and trade programs such as the US Acid Rain Program, California's Regional Clean Air Incentives Market (RECLAIM), and the Northeast's NO_x Budget Program have historically allowed trades involving only a single pollutant (Burtraw and Mansur 1999; Farrell et al. 1999; Solomon 1999; Tietenberg 1998). The basic concept of interpollutant emission trading has existed since the early 1970s (Schaltegger and Thomas 1996), and the US Chlorofluorocarbon Trading Program (Solomon 1999) has

been an example of its potential for success. Emerging provisions for IPT suggest its continued application as an instrument for increasing flexibility in achieving emissions reductions. In May 2008, the US Environmental Protection Agency (US EPA 2008) allowed limited IPT for the purpose of offsets in the Nonattainment Area New Source Review Program for $PM_{2.5}$. The final rules allows reductions in direct $PM_{2.5}$ emissions to offset precursor emissions increases, emissions reductions of one precursor to offset emissions increases of another precursor, and reductions in precursor emissions to offset direct $PM_{2.5}$ emissions increases (US EPA 2008).

IPT of ozone precursors [trading of volatile organic compound (VOC) emissions for emissions of oxides of nitrogen (NO_x)] has been very limited. Shortages of single pollutant offsets have motivated the consideration of interpollutant offsets for ozone precursors in California (US Environmental Protection Agency Region 9 Inter-Pollutant Trading Work Group 2002). The South Coast Air Quality Management District (SCAQMD) Rule 1309 (2002) in principle allows IPT on a case-by-case basis (SCAQMD 2002). IPT of ozone precursors has been approached with caution because of the difficulties in assessing the adequacy and uncertainty of trading ratios between NO_x and VOC sources and in resolving fundamental policy issues, such as environmental justice, regional transport concerns, and consistency with the objectives of State Implementation Plans (US Environmental Protection Agency Region 9 Inter-Pollutant Trading Work Group 2002; Bohning, personal communication, 2005). Provisions for IPT between ozone precursors have also been made in other states. The Maine Department of Environmental Protection's Rule 06-096 CMR 113 Growth Offset Regulation allows NO_x offset credits to be used to offset increased VOC emissions, and VOC offset credits to be used to offset increased NO_x emissions (Maine Department of Environmental Protection 1999, 2007). The New Hampshire Department of Environmental Services allows NO_x for VOC trading at a 1:1 ratio, but not vice versa, as part of its Emissions Reduction Credits (ERC) Trading Program (New Hampshire Department of Environmental Services 2003). ERCs in New Hampshire can be generated by stationary, mobile, or area sources, and are intended to improve compliance flexibility for sources subject to Reasonably Available Control Technology (RACT) requirements and to New Source Review (New Hampshire Department of Environmental Services 2003).

In a previous study, Wang et al. (2005) developed a framework for evaluating the air quality impacts of IPT between NO_x and VOC sources using the Comprehensive Air Quality Model with extensions (CAMx) Eulerian photochemical grid model (ENVIRON 2005). The framework was applied in a case study for Austin, Texas. Austin, with a population of 1.25 million people and an economic sector based on semiconductor manufacturing, software development, education, and state government, is one of thirty-three areas to enter into an Early Action Compact with the US EPA to voluntarily reduce ozone concentrations averaged over 8 h. IPT ratios (tons of NO_x emissions equivalent to a ton of VOC emissions) in Austin were, with few exceptions, independent of the source category of the emissions (i.e., mobile and area sources emissions exhibited similar impacts) and the exact choice of index that was used to determine the equivalency between NO_x and VOC emissions (i.e., trading ratios based on equivalency of maximum ozone concentration or equivalency of exposure). In contrast, trading ratios did exhibit significant (>a factor of 2) day-to-day variability, which could be attributed to daily variations in both emissions and meteorology.

The purpose of the present study is to apply the IPT modeling framework to a case study of the Houston area. In addition to its significantly greater population base of more than four million people, Houston has a dense complex of chemical production facilities and refineries that emit large amounts of VOCs including highly reactive VOCs (HRVOCs), such as ethylene, propylene, 1,3-butadiene, and isomers of butene. Strong spatial and temporal gradients in emissions of ozone precursors and daily variability in meteorological conditions exist in the Houston area. Most of the Houston area exhibits concentrations of ozone, and ozone production rates comparable to values measured in other urban areas. However, in the Houston Ship Channel region, elevated concentrations of reactive hydrocarbons are coemitted with NO_x from industrial facilities. This combination leads to substantial and rapid ozone production in this area that can be two to five times greater than other less industrialized cities and can exceed 100 ppb/h (Kleinman et al. 2002). Ozone production can vary significantly by 50 ppb or more over spatial scales as small as a few kilometers (Kleinman et al. 2002; Ryerson et al. 2003). The Texas Commission on Environmental Quality (TCEQ) is in the process of implementing an unprecedented emissions cap and trading program specifically for HRVOCs in the Houston area (Wang et al. 2007). Although IPT between VOC and NO_x emissions is not currently part of this program, pressure in the allowance market may encourage the consideration of this option in the future.

Among the most significant challenges to the development of IPT programs have been methods for trading ratio development and assessment of trading ratio variability. The intent of the present study is to address these technical issues using a case study to expand the body of knowledge about IPT available to regulators. Design and implementation of IPT programs is challenging and multifaceted. Issues such as market development and analysis, institutional roles, technological feasibility, reporting requirements and data

handling, and ecological impacts are all crucial components of trading program design and assessment that require additional study. This work will focus on modeling of air quality impacts of potential IPT.

Interpollutant emission trading model

The IPT modeling framework was developed by Wang et al. (2005). A US EPA Region 9 Work Group has examined IPT of ozone precursors for offsets and recommended the use of impact-based weighting factors or IPT ratios between NO_x and VOC emissions:

$$r = [(\partial O_3/\partial N)/\partial O_3/\partial V] \quad (1)$$

where O_3 is the concentration of ozone, $\partial O_3/\partial N$ is the increase in ozone per increase in emissions of NO_x, and $\partial O_3/\partial V$ is the increase in ozone per increase in emissions of VOCs (US Environmental Protection Agency Region 9 Inter-Pollutant Trading Work Group 2002). The IPT modeling framework developed by Wang et al. (2005) consisted of five steps:

1. Establishing an emissions trading region (i.e., a geographic area in which trading between emission sources is permitted).
2. Conducting a series of sensitivity runs with CAMx or a comparable photochemical grid model to develop an ozone productivity database for NO_x and VOC reductions from anthropogenic emission source sectors in the trading region.
3. Calculating the impact indices representing the reduction in ozone concentration or human exposure to ozone per ton of NO_x or VOC emission reduced.
4. Calculating the IPT ratios for various emission source sectors in the trading region.
5. Comparing the IPT ratios between scenarios, evaluating the effects of meteorological variability, trading region size, and selection of impact indices, and assessing implications for IPT policy.

For the previous study that focused only on Austin, trading ratios were calculated as the reciprocal of the ratio presented above (i.e., the change in the ozone concentration or other metric per increase in emissions of VOC divided by the increase in ozone per increase in emissions of NO_x). Because of NO_x disbenefits and strong variations in the sensitivity to NO_x emission reductions in the Houston area, which are discussed in detail below, trading ratios are expressed as in Eq. 1 to avoid cases where very small changes in the NO_x sensitivity lead to large changes or mathematical singularities in the trading ratios. Although at times the Austin urban core is predicted to experience NO_x disbenefits, these are largely mediated where the highest ozone concentrations and population exposure occur. NO_x reductions are consistently predicted to be more effective than the VOC reductions in the Austin area and trading ratios showed no impacts (i.e., negative values) from NO_x disbenefits.

CAMx has been selected for Texas case studies, because it is currently being used by the State of Texas for attainment demonstrations in areas that have violated the 1-h NAAQS and/or the 8-h NAAQS for ozone. The chemical mechanism used in CAMx is the Carbon Bond Mechanism version 4 (CB-IV.4) with revised PAN chemistry, radical termination mechanism, and isoprene chemistry (Adelman 1999). CAMx modeling simulations were conducted based on reductions of NO_x or VOC emissions from different source categories and trading regions, and the results were compared with those from a base case simulation without emission reductions to quantify ozone productivities for each scenario. Emission inventories were divided into four source categories: area sources and nonroad mobile sources, on-road mobile sources, point sources, and biogenic sources. Emission trading involving biogenic sources was not considered. Sensitivity studies were conducted in which NO_x or VOC emissions from each anthropogenic source category were reduced. The magnitudes of the emission reductions were selected such that a substantial, but relatively consistent, level of reduction could be made from each source category in each trading region.

To address whether the choice of air quality impact would influence trading ratios, a variety of impact metrics have been considered. Metrics based on maximum daily 8-h ozone concentrations, time-integrated area of exceedance above a threshold ozone concentration, and total daily population exposure are described below (Durrenberger et al. 1999; Wang et al. 2005). Although ozone concentration is the most significant metric from a regulatory context, examining the impacts on other metrics, most notably population exposure, facilitates broader evaluation of trading programs and may be particularly relevant to concerns about environmental equity.

Impact indices were calculated as the change in a metric that occurs in an area if the emissions decrease by 1 ton of NO_x or VOC per day and were used as the basis for developing IPT ratios.

Maximum 8-h ozone concentration

$$M_{\max 8} = \max_{g,h}\{c_{g,h}\}$$

where $c_{g,h}$ is the modeled ozone concentration (in ppb) in grid cell g at hour h.

This metric was calculated by examining all ground-level grid cells in the Houston area during each episode day and selecting the maximum 8-h ozone concentration.

Time-integrated geographic area of exceedance above a threshold ozone concentration of 85 ppbv

$$M_{\text{time area}} = \sum_h \sum_g a_g \delta_{g,h}$$

where a_g is the area of grid cell g (in km^2) and

$$\delta_{g,h} = \begin{cases} 0, c_{g,h} \le 85, \\ 1, c_{g,h} > 85 \end{cases}$$

$$\delta_{g,h} = \{\delta_{g,1}, \delta_{g,2}, \delta_{g,3}, \ldots \delta_{g,24}\}$$

This metric was calculated by examining the 8-h ozone concentrations in each ground level grid cell in the Houston area for each hour of each episode day and determining if the cells exceeded the threshold 8-h ozone concentration of 85 ppb. The areas of all cells exceeding the threshold were then summed for each hour. The areas for each hour were then summed over the day. This metric considered both the temporal extent and spatial extent of the exceedance, but did not depend on the extent to which the ozone concentration exceeded the threshold. Although a threshold ozone concentration of 85 ppb was used in this study, it could be set to a different value in response to local interests or changes in the National Ambient Air Quality Standard.

Total geographic area of exceedance above a threshold ozone concentration of 85 ppbv

$$M_{\text{total area}} = \sum_g a_g \max\{\delta_{g,h}\}$$

Wang et al. (2005) found that the variability in trading ratios based on this metric was particularly high due to the relatively small number of grid cells involved in the calculation of the metric and its discrete nature. Similar results were obtained in this study for Houston. Consequently, this metric is not recommended for regulatory analyses, and trading ratios based on this metric are not included in the results presented below.

Total daily population exposure

$$M_{\text{pop}} = \sum_h \sum_g p_g s_{g,h}$$

where $s_{g,h} = \begin{cases} 0, c_{g,h} \le 85, \\ c_{g,h} - 85, c_{g,h} > 85 \end{cases}$ and p_g is the population density in each grid cell.

This metric was calculated, for each grid cell, by multiplying the population density by the ozone concentration over the threshold (shown as 85 ppb). The sum is taken over the total area of the eight counties, and then summed over hours. M_{pop} is an overall measure of total daily ozone exposure over the threshold within the area of interest. It is responsive to the temporal and spatial extent of ozone exceedances, as well as the exposure level.

An impact index is the measure of the change in a metric that occurs if the emissions decrease by one ton of NO_x or VOC per day:

$$\text{Ozone Impact Index } (m_i) = \frac{\text{Case Study Metric} - \text{Base Case Metric}}{\text{Tons of } NO_x \text{ or VOC reduced/day}} \quad (2)$$

IPT ratios between pairs of source categories were calculated for each trading region. For example, the trading ratio between NO_x reductions from area and nonroad sources and VOC reductions from mobile sources for impact index, m_i, in a trading region is

$$\text{Trading ratio} = \frac{m_i \text{ from on} - \text{road mobile source } NO_x \text{ reduction}}{m_i \text{ from area and nonroad mobile source VOC reduction}} \quad (3)$$

IPT model application to Houston, Texas

A description of the modeling episode and emissions inventory to be used for the Houston case study is presented below.

Modeling episode and domain

The eight-county Houston/Galveston/Brazoria ozone nonattainment area and the modeling domain for the episode, which consists of a nested 32/16/4 km grid, are shown in Fig. 1. Figure 2 shows the population density in the eight-county Houston/Galveston/Brazoria area. Conceptual models of ozone formation in the Houston area are provided by Nielsen-Gammon (2002) and Texas Commission on Environmental Quality (TCEQ) (2002). The TCEQ developed an August 22–September 6, 2000, Base Case photochemical modeling episode to support the development of its State Implementation Plan for the region.

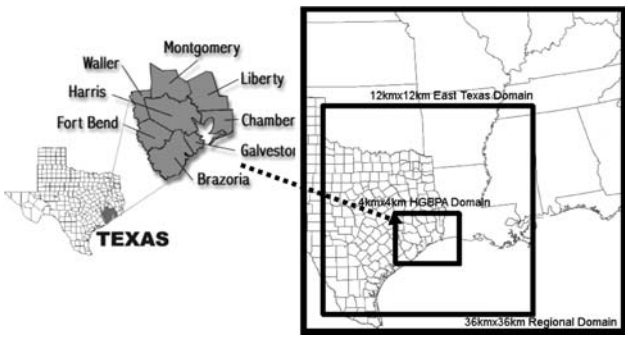

Fig. 1 The eight-county Houston/Galveston/Brazoria ozone nonattainment area and modeling domain

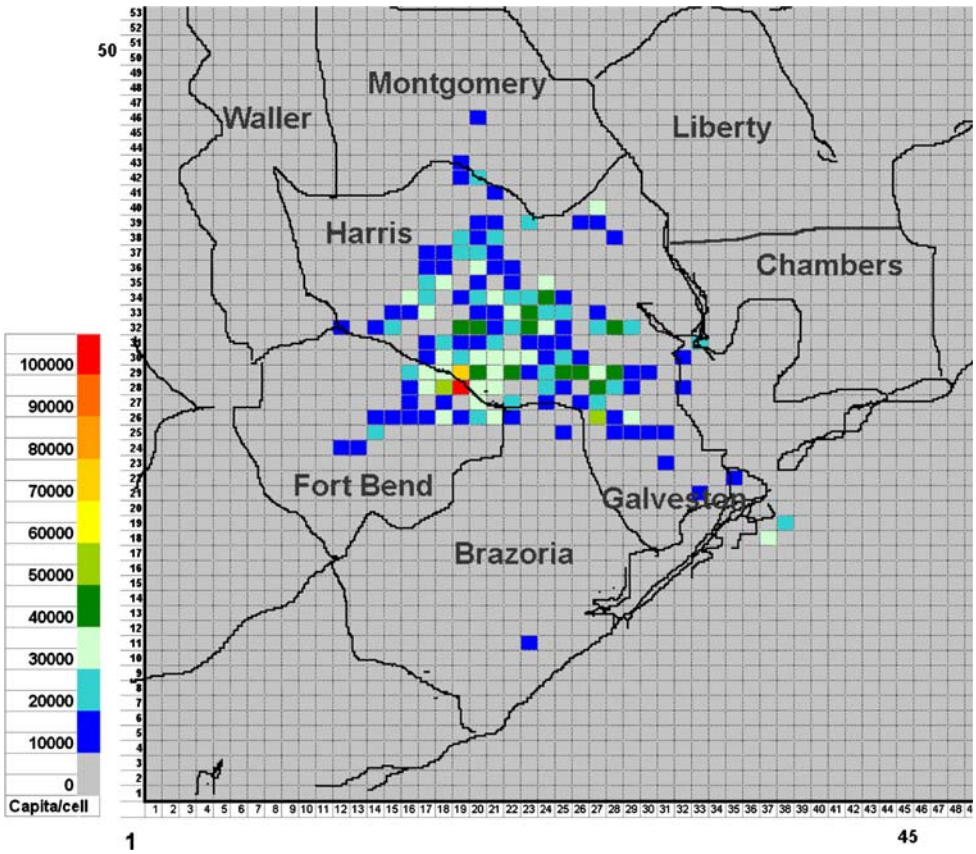

Fig. 2 Population (per 4 km by 4 km grid cell) in eight-county Houston/Galveston/Brazoria ozone nonattainment area

Meteorological conditions during the episode are described by Macdonald and Roberts (2002). This episode includes the period of the Texas Air Quality Study 2000 (http://www.utexas.edu/research/ceer/texaqs/), which provided an extensive database of surface and airborne measurements for model performance evaluation in southeast Texas (TCEQ 2004). The modeled period was used in the designing control strategies for meeting the NAAQS for ozone, with concentrations averaged over 1 h. All the simulations reported in the present study use a 2007 emission inventory (the attainment demonstration inventory) as a starting point (TCEQ 2004).

Emission inventories

Figure 3a–d shows the magnitude and spatial distribution of projected 2007 elevated point source NO_x emissions, low-level anthropogenic (i.e., area, mobile, and point) and biogenic NO_x emissions, elevated point source VOC emissions, and low-level VOC emissions, on a typical weekday. Elevated point source NO_x and VOC emissions are concentrated in the Houston Ship Channel industrial complex with several large point sources of NO_x emissions in Fort Bend and Brazoria Counties. Low level NO_x emissions are mainly from mobile sources concentrated in the downtown Houston urban core (within Harris County) and spreading outwards along major transportation corridors. Low-level anthropogenic VOC emissions occur in the Ship Channel and downtown Houston. Biogenic VOC emissions extend from Harris County to northeast Texas. Table 1 shows a summary of projected 2007 daily NO_x and VOC emissions from anthropogenic emission source sectors for each county in the nonattainment area. Harris County accounts for more than half of the NO_x and VOC anthropogenic emissions in the eight-county area, with NO_x emissions dominated by mobile sources and VOC emissions dominated by industrial point sources and area sources.

One simulation of the attainment demonstration without any additional emission reductions (base case) was conducted. Eight sensitivity runs were conducted to generate the 8-h average ozone productivity database for Houston. The eight runs included NO_x and VOC reductions, respectively, of 25 tons/day (tpd) from anthropogenic, mobile, area, and point sources in the eight-county area.

Results and discussion

IPT ratios for the eight-county Houston area are reported in Table 2 and Fig. 4. A total of 16 ratios are reported, representing all of the possible combinations of the four NO_x emission categories (on-road mobile, point, area/nonroad,

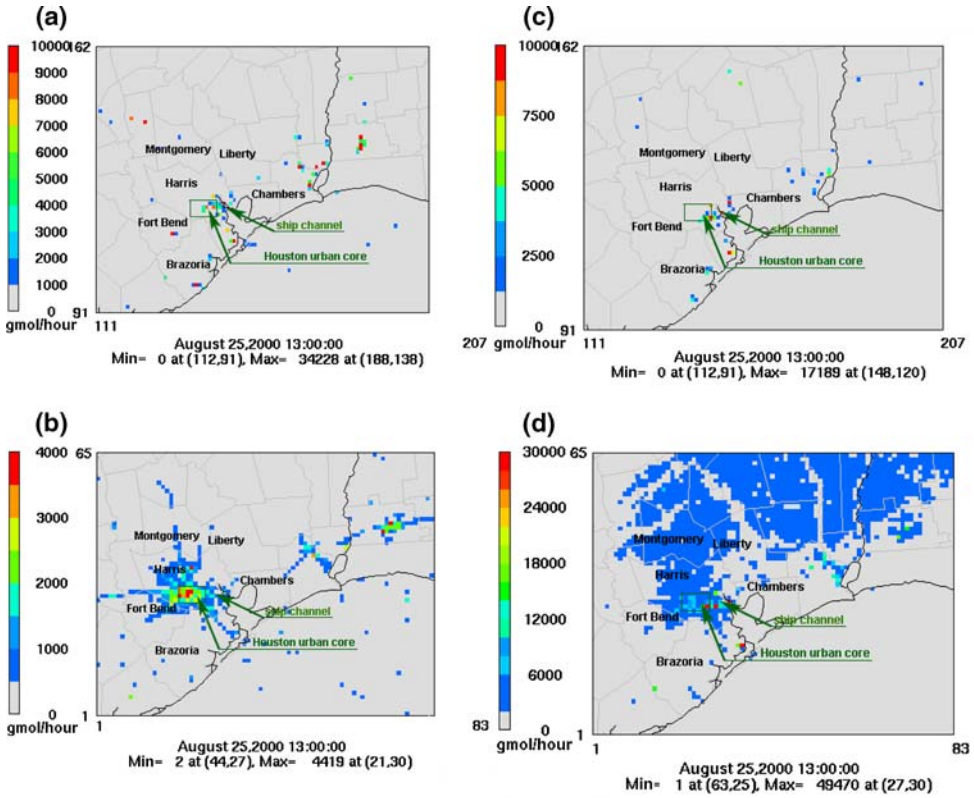

Fig. 3 Emissions of **a** elevated point source NO_x, **b** low-level anthropogenic and biogenic NO_x, **c** elevated point source VOC, and **d** low-level anthropogenic and biogenic VOC, on a typical weekday in 2007 (August 25)

Table 1 Daily 2007 NO_x and VOC emissions from anthropogenic sources in the eight-county Houston area (August 22, typical weekday)

County name	Emissions (tons/day)							
	Area		Mobile		Point		Total anthrogenic emission	
	NO_x	VOC	NO_x	VOC	NO_x	VOC	NO_x	VOC
Brazoria	10.99	19.14	8.97	2.98	29.77	31.30	49.73	54.43
Chambers	4.81	4.30	4.24	1.60	2.96	5.10	12.01	11.01
Fort Bend	9.18	22.18	16.20	7.12	13.05	3.23	38.43	32.54
Galveston	6.25	14.85	6.04	2.92	29.00	38.27	41.30	56.04
Harris	59.10	132.48	113.81	53.45	95.13	147.69	268.04	333.63
Liberty	3.00	6.22	3.15	1.54	3.17	2.17	9.32	9.93
Montgomery	5.02	15.23	13.21	5.35	3.38	2.36	21.60	22.94
Waller	2.48	3.44	3.72	1.67	2.78	0.81	8.97	5.91
Eight-county total	100.84	217.84	169.34	77.64	179.23	230.95	449.41	526.42
Harris	59.10	132.48	113.81	53.45	95.13	147.69	268.04	333.63
Seven-county total	41.74	85.36	55.53	24.19	84.10	83.25	181.37	192.79

and total anthropogenic) and four VOC emission categories. Values are presented for each day of the modeling episode, except for the last day, when it is not possible to calculate 8-h averaged concentrations for the entire 24-h period. Negative IPT ratios indicate NO_x disbenefits or increases in a metric due to NO_x reductions.

Trading ratios among various source categories are generally tightly clustered on and between many modeling days; this is a desirable result suggesting that trades within and between emission sectors could have similar outcomes, which in principle should increase flexibility in the trading market. Wang et al. (2005) found that trades between mobile and area sources in Austin were tightly clustered on most episode days and for most metrics. However, IPT ratios in Houston show significant variability between some episode days, source categories, and metrics; for

Table 2 Median and standard deviation of interpollutant trading ratios for the Houston area for the daily maximum ozone concentration, time integrated area of exceedance, and population exposure metrics

Metric	Statistic	Interpollutant trading ratios																All
		8/22	8/23	8/24	8/25	8/26	8/27	8/28	8/29	8/30	8/31	9/1	9/2	9/3	9/4	9/5	9/6	
Daily maximum 8-h ozone concentration	Median	1.12	0.40	2.55	0.96	3.58	8.76	6.85	3.34	0.23	0.64	5.18	−0.46	2.25	3.56	4.34	7.44	2.39
	Standard deviation	0.18	0.11	0.85	0.38	1.27	4.22	2.65	1.32	0.24	0.07	3.50	1.06	1.12	2.37	2.15	2.99	3.43
Time-integrated area of exceedance	Median				1.25	2.25			3.00	0.15	6.67	6.18	2.00	1.40	17.67	7.81		2.74
	Standard deviation				0.33	1.12			3.13	0.15	5.17	2.20	1.66	0.25	5.18	7.06		6.28
Population exposure	Median				1.12	1.79			2.77	−0.73	3.03	2.04	0.49	2.01	7.37	0.08		1.65
	Standard deviation				0.27	0.27			0.53	0.41	3.24	1.47	1.36	0.48	3.87	1.03		2.99

The overall trading ratio over all episode days and metrics was 2.04 ± 4.45

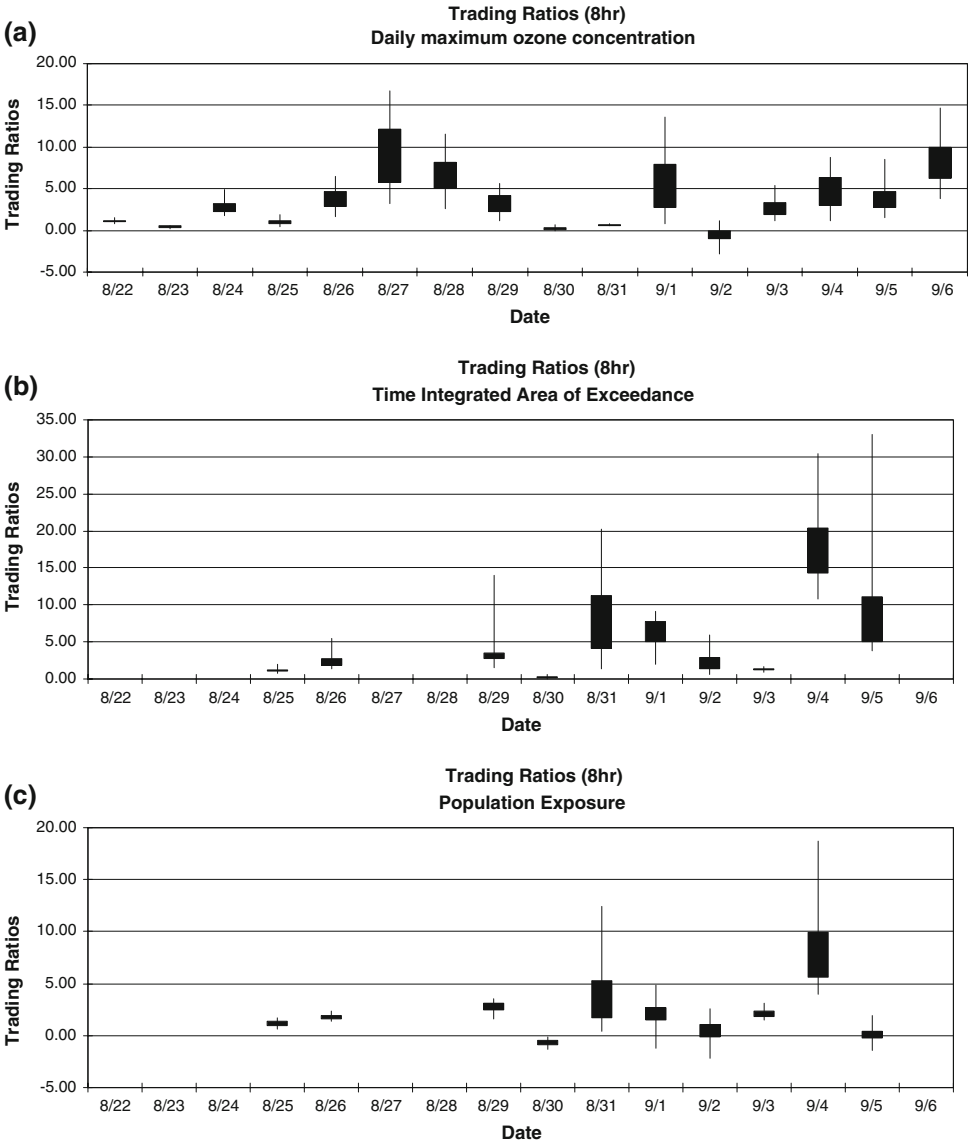

Fig. 4 Interpollutant trading ratios based on **a** daily maximum ozone concentration, **b** time-integrated area of exceedance, and **c** population exposure for trades involving mobile, area, point, and anthropogenic sources in the Houston area. *Boxes* represent the band between 25th and 75th percentiles

example, trading ratios for the population exposure metric on August 30 (−0.73 ± 0.41), September 2 (0.49 ± 1.36), and September 5 (0.082 ± 1.03) were markedly lower than the median value of 1.65 ± 2.99, and were much lower than the ratio on September 4, which was 7.37 ± 3.87. The daily variability in trading ratios suggest that annual and seasonal variability in IPT ratios should be evaluated in addition to episodic variability in the setting of safety factors. The overall trading ratio calculated over all metrics and episode days is 2.04 ± 4.45 (median ± standard deviation), indicating that, similar to the results for Austin, NO_x emission reductions are generally more effective than VOC reductions for reducing ozone concentrations averaged over 8 h (approximately 2 tons of VOC emission reductions lead to the same decrease in the performance metrics as 1 ton of NO_x emission reductions). These results are consistent with control strategies pursued in the State Implementation Plan for Houston, which generally target NO_x emissions reductions, with the addition of reductions of highly reactive VOCs from industrial sources.

Trading ratios for the three metrics across all episode days were 2.39 ± 3.43 for the daily maximum 8-h ozone concentration metric, 2.74 ± 6.28 for the time-integrated area of exceedance metric, and 1.65 ± 2.99 for the population exposure metric, and median values were within a factor of two. However, Fig. 5 compares IPT ratios for different metrics in the eight-county Houston area; the same IPT ratios are compared on the same days. Correlations between the metrics are poor, which is not a desirable result. It increases the complexity of trading program design (e.g., minimizing population exposure versus maximum daily ozone concentrations) and highlights the difficulty of predicting the benefits of trades. Spatial gradients in emissions, ozone concentrations, and the population distribution have pronounced impacts on the variability between metrics. In Austin, which has anthropogenic emissions dominated by mobile and area sources, daily maximum 8-h ozone concentrations generally occur within close proximity to areas that have the highest population densities; Wang et al. (2005) found that metrics were generally well-correlated. In contrast, Houston has a dense industrial complex distinct from its largely mobile and area source dominated urban core. High 8-h ozone concentrations may not be spatially correlated with areas of

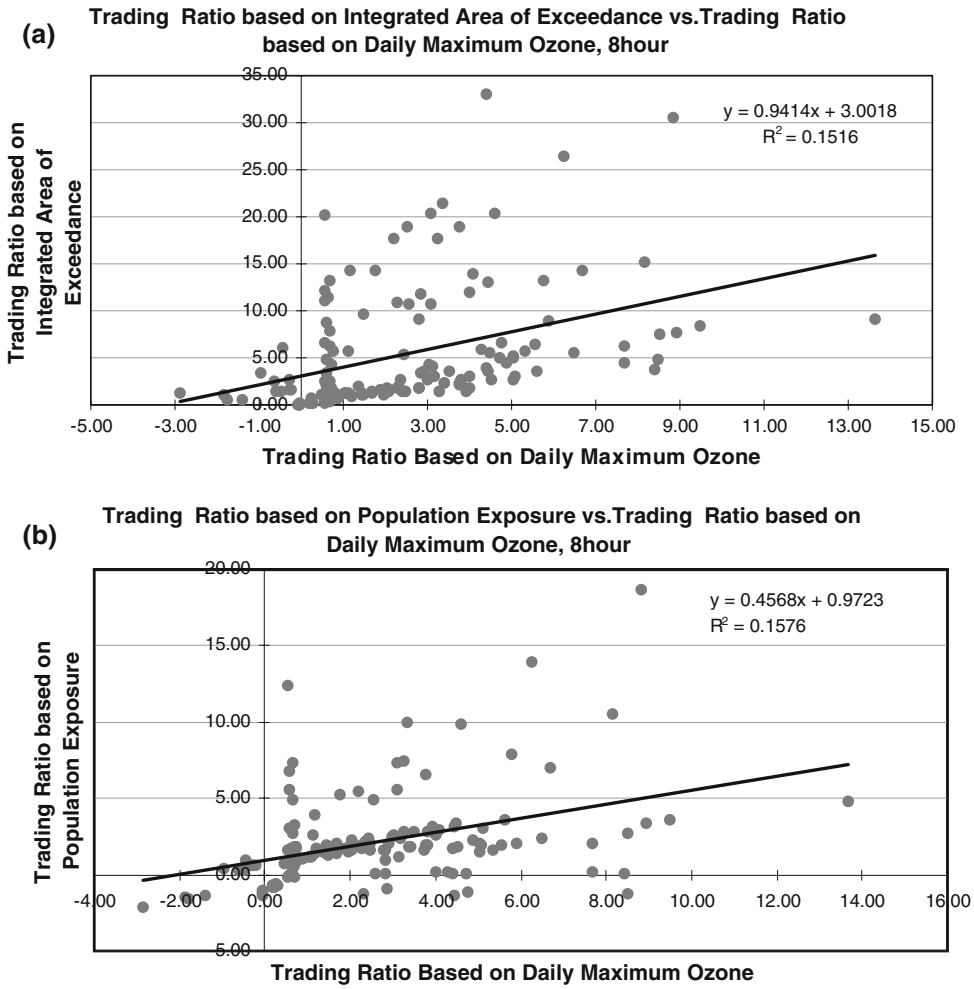

Fig. 5 Comparisons of IPT ratios for different metrics in the Houston area: **a** time-integrated area of exceedance versus daily maximum 8-h ozone concentration; **b** population exposure versus daily maximum 8-h ozone concentration. The same IPT ratios for the same days are compared for different metrics

greatest population density, resulting in poor correlation between these metrics.

The CAMx model has a process analysis option that can be used to identify chemical and physical process rates that lead to predicted concentrations of ozone and other species over a subvolume of the modeling domain. The process analysis program calculates, for every species, rates of chemical and physical processes, such as horizontal and vertical pollutant fluxes crossing cell boundaries, chemical production and consumption rates, emission rates, deposition rates, and initial and final concentrations. Process analysis was implemented on several episode days, August 26, August 30, and September 5, to improve the understanding of the root causes for variations in trading ratios among different episode days and metrics. The process analysis subdomains shown in Fig. 6 for August 26 and September 30 and in Fig. 7 for September 5 were centered on the regions with peak ozone concentrations. Another process analysis subdomain that included an area associated with high emissions from the urban core and from a portion of the industrial area, an emission source region, was also established on August 30.

As described by Vizuete et al. (2008) and Jefferies and Tonnesen (1994), the addition of process analysis to a photochemical model results in an Integrated Reaction Rate file that provides integrated rates for each reaction in the chemical mechanism over each output time step. Reaction cycle diagrams can be created that summarize the cycling of nitrogen oxides, hydroxyl radical, and ozone formation processes (specifically describing radical initiation, propagation, and termination, as well as NO emission, oxidation to NO_2, and photolysis to O_3 and NO as a linked set of processes with feedbacks) (Vizuete et al. 2008). The NO chain length represents the average number of times each newly emitted NO is cycled before being lost in termination reactions and is calculated based on the nitrogen propagation factor (P_{NO}) or the probability than an NO_2 molecule will be photolyzed rather than lost by chemical reaction (Jefferies and Tonnesen 1994):

$$\text{NO chain length} = 1/(1 - P_{NO})$$

Similarly, the OH chain length is the average number of times each new OH radical is cycled or recreated before termination and is based on a hydroxyl radical propagation factor (P_{OH}). The relative changes in the NO chain length in urban airsheds can provide indications of transitions between NO_x- and VOC-limited conditions. Under NO_x-rich conditions, the primary radical termination reaction is

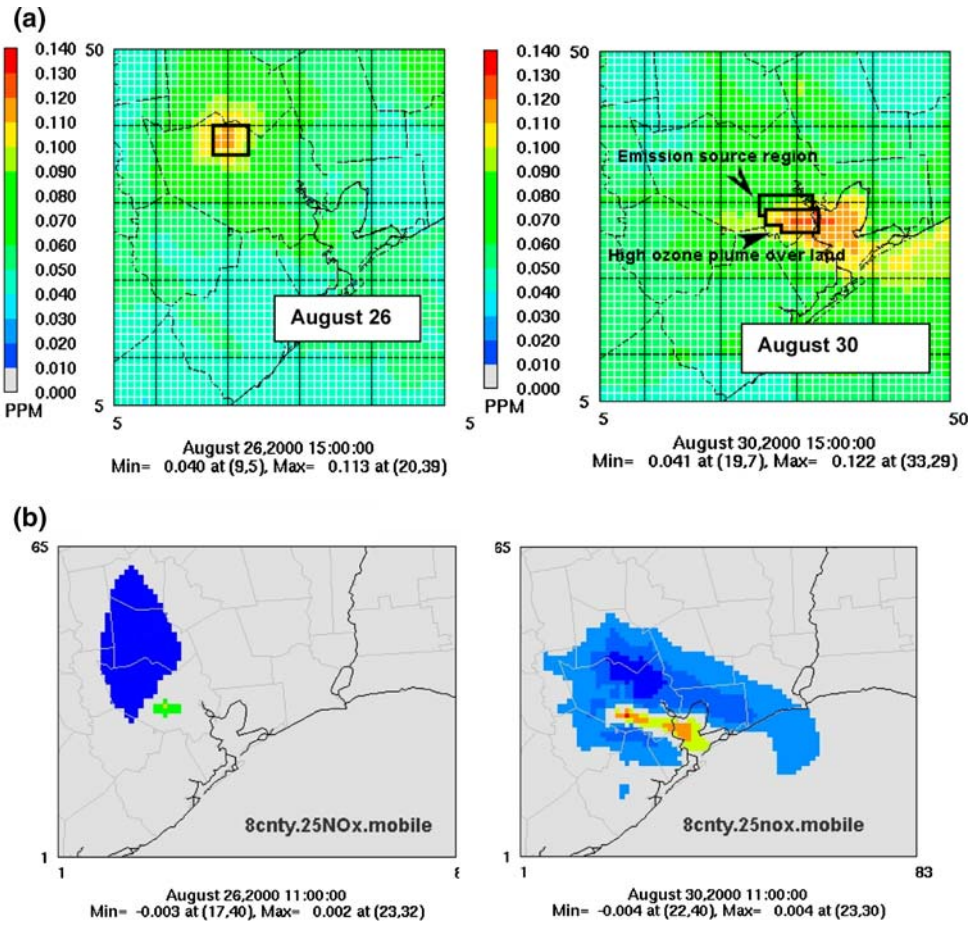

Fig. 6 **a** The spatial distributions of ozone concentrations at 1500 hours and subdomains used in the process analysis on August 26 (*left*) and August 30 (*right*). **b** Differences in eight-hour ozone concentrations when NO_x emissions from mobile sources are reduced by 25 tons/day in the eight-county area and the base case on August 26 (*left*) and August 30 (*right*). Difference = concentration of ozone (trading case − base case)

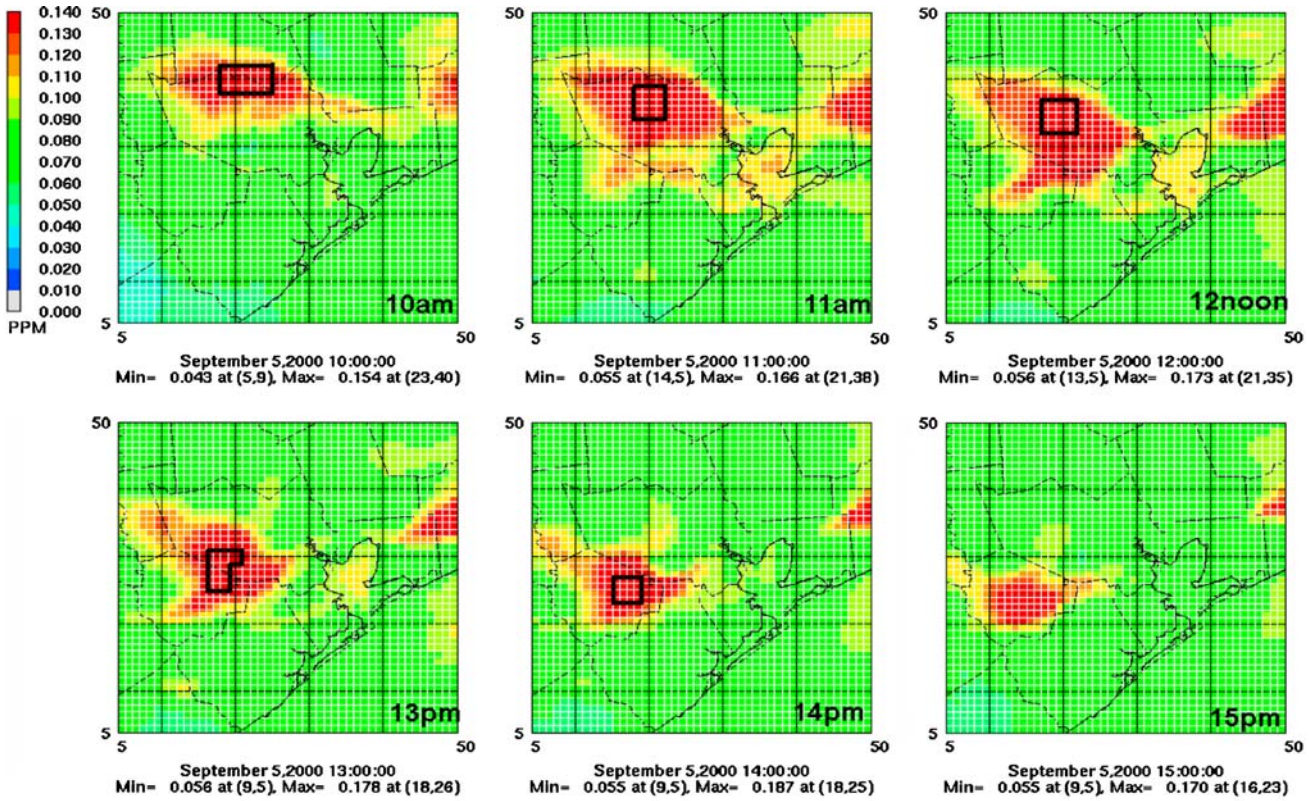

Fig. 7 Ozone plume movement and process analysis subdomains for September 5

nitric acid formation; P_{NO} and, consequently, the NO chain length, are lower than that under NO_x-limited conditions. Under NO_x-limited and VOC-rich conditions, hydrocarbon reactivity is highly relative (sum of k^i_{OH} [VOC_i] over all VOC) to the OH termination reaction frequency (sum of k^i_{OH} [NO_2] plus other radical loss pathways) (Vizuete et al. 2004, 2008). Table 3 shows the OH and NO chain lengths during the chemical process of ozone formation on each episode day when process analysis was implemented. A typical OH chain length in an urban air shed is 3.3 and a more reactive mixture would show a chain length in excess of 4 (Jefferies and Tonnesen 1994; Vizuete et al. 2004). A NO chain length in excess of 3 is generally considered more reactive (Jefferies and Tonnesen 1994; Vizuete et al. 2004).

On August 26, ozone formed in the Ship Channel area in the morning, and southeasterly winds advected ozone to the northwest of the Houston urban core and the Ship Channel in the afternoon at 1500 hours when the peak ozone concentration occurred. Only a small area (eight 4 km × 4 km grid cells shown in Fig. 6) in northwest Harris County is in exceedance of the threshold ozone concentration on August 26. The ozone plume avoids the most densely populated area. The OH and NO chain lengths of 2.71 and 3.93, respectively, on August 26 in Table 3 indicate moderate reactivity. NO_x-disbenefits occurred in a small area in downtown Houston area in response to reductions in area/nonroad source as well as mobile source emissions. Mobile source reductions, shown in Fig. 6, occurred primarily in a

Table 3 Radical and NO_x chain length of ozone production in the process analysis subdomains

Episode day	PA domain	OH chain length	NO chain length
August 26	High ozone plume	2.71	3.93
August 30	Ship Channel emission sources	3.46	1.86
	High ozone plume over land	3.37	3.51
September 5	High ozone plume at 10 a.m.	2.99	4.71
	High ozone plume at 11 a.m.	3.06	2.5
	High ozone plume at 12 a.m.	3.19	2.48
	High ozone plume at 13 p.m.	3.55	2.23
	High ozone plume at 14 p.m.	3.44	5.38

highly VOC-limited area (downtown Houston area) and, consequently, were associated with a slightly larger area of NO_x-disbenefits than area source reductions. The small area and short time of occurrence of NO_x-disbenefits in downtown Houston did not significantly affect the metrics across the source categories. Thus, differences in trading ratios between source categories were not large, and trading ratios behaved reasonably consistently between metrics.

In contrast to August 26, stagnation occurred almost throughout the day on August 30 and ozone formation is mainly due to local photochemical production. On this day, NO_x-disbenefits occurred in a large area over downtown Houston and Galveston Bay, shown for mobile sources as an example in Fig. 6, and last for a considerably longer period of time due to stagnation. The NO chain length of 1.86 on August 30 indicates that conditions in this subdomain, the emission source region, are VOC-limited. Trading ratios on this day tend to be lower (or even negative for the population exposure metric under extreme VOC-limited conditions) than a more NO_x-limited day such as August 26.

On September 5, differences in trading ratios between the metrics in Table 2 are considerably greater than on the other two days (i.e., median $\pm$ standard deviation for the population exposure is 0.08 ± 1.03, as compared to 4.34 ± 2.15 for the daily maximum ozone concentration and 7.81 ± 7.06 for the integrated area of exceedance metrics). Figure 7 shows the formation and movement of the high ozone plume between 1000 and 1500 hours on this day. In contrast to the other episode days, ozone exceedances occurred relatively early in the morning on September 5th and traverse large portions of the eight-county area. The high ozone plume forms in northwest Harris County and a northeasterly wind transports the plume across Harris County to Fort Bend County where the maximum daily ozone concentration occurs at 1400 hours. Process analysis indicates that during transport of the plume, the OH/NO cycles switch from NO_x-limited conditions at 1000 hours (2.99 OH chain length and 4.71 NO chain length) to more VOC-limited conditions at 1100 hours (3.06 OH chain length and 2.50 NO chain length) through 1300 hours (3.55 OH chain length and 2.23 NO chain length) and then return to more NO_x-limited conditions again at 1400 hours (3.44 OH chain length and 5.38 NO chain length). As shown in Fig. 7, at 1200 through 1300 hours, the plume traverses the area with the densest population and the population metric is most responsive to emission reductions. The VOC-limited conditions during this time period lead to lower trading ratios for this metric, since reductions of VOCs are generally more effective than that under less VOC-limited conditions.

Conclusions

Trading ratios in Houston are relatively consistent on many episode days with an overall value of 2.04 ± 4.45 tons of VOC emission reductions required to have the same effect as a reduction of 1 ton of NO_x emissions (median $\pm$ standard deviation). However, IPT ratios based on different metrics are weakly correlated in Houston. As discussed above, poor correlation between metrics is not desirable and presents complexities for trading program design. Careful consideration must be given to the equity of trades with respect to population exposure and the construction of safety factors. NO_x disbenefits have a particularly important influence on the variability in IPT ratios between source categories and metrics on some episode days. Frequent and geographically large areas of NO_x disbenefits challenge the use of IPT in a region. Further work should focus on the relative air quality and economic benefits of IPT versus conventional command and control strategies in the Houston area, the influence of geographic trading zones within and between emission source categories on the correlation between metrics, and the need for seasonal modeling studies to determine the overall frequency with which NO_x disbenefits become important in the assessment of IPT impacts.

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